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Research Article

Catalytic Performance for Hydrocarbon Production from Syngas on the Promoted Co-Based Hybrid Catalysts: Influence of Pt Contents

Suk-Hwan Kang[1,*], Jae-Hong Ryu[1], Jin-Ho Kim[1], Hyo-Sik Kim[1], Hee Chul Yang[2], Dong Yong Chung[2]

[1]Institute for Advanced Engineering (IAE), 633-2 Baegam-myeon, Cheoin-gu, Yongin-si, Gyeonggi, 449-863, Korea
[2]Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 305-353, Korea

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Abstract

Fischer-Tropsch synthesis (FTS) reaction from syngas was investigated on the Pt-promoted cobalt-based hybrid catalysts prepared by co-precipitation method in a slurry of ZSM-5 (Si/Al=25). The hybrid catalysts were compared with each other for the different content of Pt as a promoter and are characterized using BET, XRD, H_2-TPR and NH_3-TPD. Their physicochemical properties were correlated with the activity and selectivity of the catalysts. As results, all hybrid catalysts show the C_5-C_9 yield (%) higher than that of Co-Al_2O_3/ZSM-5 catalyst. The Pt-promoted hybrid catalysts were found to be more promising towards production of the hydrocarbons of gasoline range and over C_{10}.

Keywords: Syngas; Fischer-Tropsch synthesis; Hybrid catalyst; ZSM-5

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1. Introduction

Fischer-Tropsch synthesis (FTS), using syngas (including CO and H_2) derived from coal, natural gas, bio-gas, or other carbon-containing materials, has recently been received considerable attention as an alternative efficient method for synthesizing clean fuels and useful chemicals [1]. In general FTS, cobalt-based catalyst was operated at temperature in the range of 210-250 °C, the main products are composed of the diesel, food grade paraffin and specialty lubricants obtained after proper upgrading processes such as hydrocracking, hydrodewaxing or isomerization reaction. On the other hand, iron-based catalyst operating at temperature around 350 °C yields the premium petrochemical naphtha and *α*-olefins, as the main products [2,3].

The polymerization mechanism (known as Anderson-Schulz-Flory (ASF) distribution) in FTS reaction is inherently found to show a wide-range of hydrocarbon distribution from

* Corresponding Author.
E-mail: shkang@iae.re.kr (Kang, S.H.)
Telp.: +82-31-330-7880

methane to heavy waxy product and the extent of ASF distribution is represented by the chain growth probability. Therefore, the hydrocarbon selectivity towards gasoline range products during FTS reaction is generally known to be limited to a maximum of 48 mol% [4].

To obtain branched hydrocarbons selectively, especially for high-octane gasoline production, many efforts have been carried out intensively by modifying cobalt-based catalysts. Some researchers have investigated the hybrid or composite systems consisting of cobalt component as the FTS catalyst and zeolite as the cracking catalyst by using the following representative methods; (i) cobalt-based catalyst mixed physically with zeolites [5-7], (ii) zeolite supported cobalt-based hybrid catalyst prepared by wet-impregnation method [8], (iii) membrane-coating using zeolite component on the supported Co/SiO_2 catalyst [9-12], and (iv) cobalt-based hybrid catalyst co-precipitated in a slurry of zeolite [13]. However, the enhancement of Co reducibility on Pt as a promoter has been reported for several supports (e.g. SiO_2, TiO_2, ZrO_2) though it seems especially pronounced in the case of Al_2O_3 [14].

In the present paper, we report the catalytic activity and product distribution obtained from FTS reaction using $Co-Al_2O_3-xPt/ZSM-5$ (Si/Al=25) catalysts with four different Pt content to elucidate the reducibility and acidity of hybrid catalysts with or without Pt as promoter for the production of gasoline range (C_5-C_9) and C_{10+} hydrocarbons from syngas. The objective of this work is to find out its catalytic performance during FTS reaction on hybrid catalysts with increasing Pt content.

2. Materials and Method

Fischer-Tropsch synthesis (FTS) reaction for the direct production of gasoline range hydrocarbons (C_5-C_9) from syngas was investigated on cobalt-based catalysts with promoter as Pt. The catalysts were synthesized by co-precipitation method in an aqueous solution containing Co and Al metal precursors (cobalt nitrate and aluminum nitrate with the weight ratio of Co/Al_2O_3 = 20/100) and Na_2CO_3 solution as a precipitating agent at 70 ^oC in a slurry of ZSM-5 (Si/Al=25). The precipitate was further aged for 3 h at 70 ^oC followed by calcination at 500 ^oC for 5 h. The same procedure was followed for the different contents of Pt using the nitrate precursor. Finally, the ratios of cobalt and Pt metal components to that of ZSM-5 in the hybrid catalysts were fixed at 20/30 and 0.05 (or 0.1, 0.3, 0.5)/30 by weight. The hybrid catalysts are noted as $Co-Al_2O_3-xPt/ZSM-5$ (x is 0.05, 0.1, 0.3 and 0.5).

Catalytic activity test was carried out in a tubular fixed bed reactor. Prior to the reaction, the catalyst was reduced at 400 ^oC for 12 h in a flow of 8 % H_2 balanced with nitrogen. After reduction, the synthesis gas (H_2/CO = 2) was fed into the reactor [1]. The FTS reaction was carried out subsequently under the following reaction conditions; T = 240 and 260 ^oC, P = 2.0 MPa and SV = 4,000 mL/g_{cat} h. The effluent gas from the reactor was analyzed by an online gas chromatograph (Young Lin Acme 6000 GC) employing GS-GASPRO capillary column connected with flame ionized detector (FID) for the analysis of hydrocarbons and a Carboxen-1000 packed column connected with TCD for the analysis of carbon oxides, hydrogen, methane and internal standard gas of Ar.

3. Results and Discussion

In previous studies, we highlighted the influence of promoter on the activity of co-precipitated $Co-Al_2O_3$-(promoter)/ZSM-5 hybrid catalysts. In the case of Ru and Pt as promoter, the reducibility of cobalt species and the density of weak acid sites were observed to be higher, thus increasing the CO conversion and C_5-C_9 selectivity [13].

3.1 Textural properties and cobalt particle size of hybrid catalysts

The BET surface area, pore volume and average pore diameter are summarized in Table 1. However, surface area of the promoted catalysts slightly increased compared to that of Co/ZSM-5 catalyst. Large specific surface area and pore volume of the catalyst affects its reducibility and the catalytic performance during FTS reaction.

In order to understand the dependence of activity for the promoted Co/ZSM-5 hybrid catalysts on their physicochemical properties, all hybrid catalysts before the reaction show the characteristic reflection peak at 2θ = 36.8^o due to the presence of Co_3O_4 phase, as seen in Figure 1. The particle size of Co_3O_4 is calculated by using the X-ray line broadening method with the help of Scherrer's equation. The crystallite size of Co_3O_4 for the hybrid catalysts promoted by Pt content (0.05, 0.1, 0.3 and 0.5) is 10.8, 10.6, 10.4 and 9.6 nm, respectively. In general, the cobalt particle size of promoted $Co-Al_2O_3/ZSM-5$ catalysts is lower than 10.9 nm of $Co-Al_2O_3/ZSM-5$ catalyst. The smaller particle size of the easily reducible cobalt species uniformly distributed inside the relatively larger pores are reported to be responsible for the higher activity of promoted Co-Al_2O_3/ZSM-5 hybrid catalysts [2].

3.2 Temperature-programmed analyses (H_2-TPR and NH_3-TPD)

TPR experiments were carried out to understand the reduction behavior of cobalt oxides which is important since metallic cobalt surface sites are responsible for FTS activity. The reduction profiles of calcined hybrid catalysts are shown in Figure 2, and the degree of reduction is also calculated from H_2 consumption up to 300 ^oC in TPR runs by dividing it with total amount of H_2 consumption as summarized in Table 2. TPR profiles on hybrid catalysts exhibit two distinct reduction peaks which could correspond to the two-step reduction $Co_3O_4 \rightarrow CoO$ and $CoO \rightarrow Co^0$ at below 422 ^oC, and they are observed at lower temperature than that of Co-Al_2O_3/ZSM-5 catalysts [15]. The first reduction peak is generally attributed to the reduction of Co_3O_4 to CoO and the second peak is assigned to the reduction of CoO to metallic cobalt. TPR profiles of three promoted Co-Al_2O_3/ZSM-5 (including Pt of 0.1, 0.3, and 0.5) catalysts also show a distinct peak at below 203-204 ^oC and an intense second peak at a maximum temperature (T_{max}) around 292-298 ^oC which could be assigned to complete reduction of cobalt oxides to metallic cobalt. The peak intensity at higher temperature region around 700 ^oC suggests the possible transformation of cobalt oxide to the inactive cobalt silicates on catalysts [16,17].

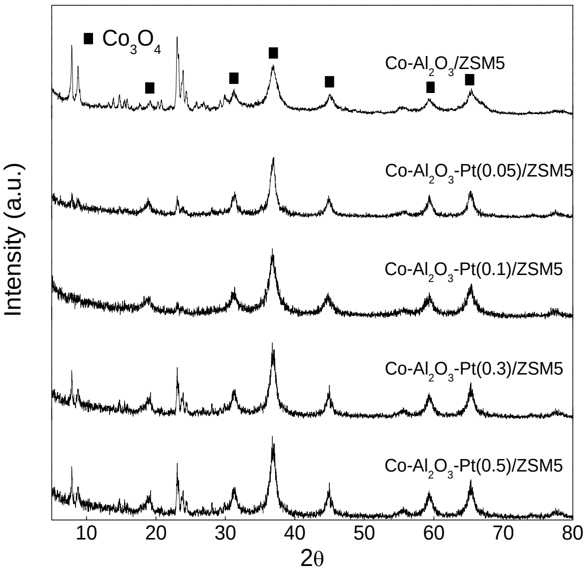


Figure 1. XRD patterns of the calcined hybrid catalysts

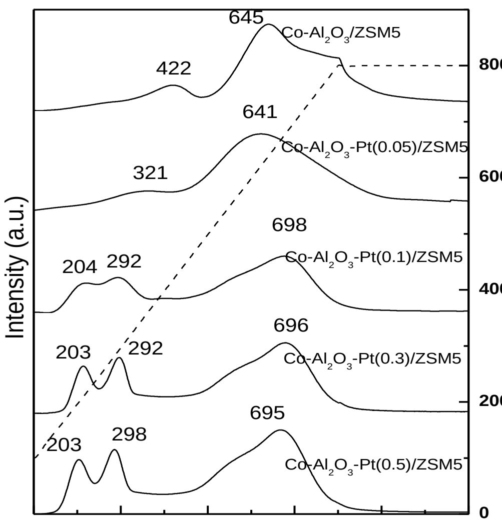


Figure 2. H_2-TPR profiles of fresh Co-Al_2O_3/ZSM-5 and Pt promoted Co-Al_2O_3/ZSM-5 catalysts

Table 1. Physical properties and particle size of Co-Al_2O_3-promoter/ZSM-5 catalysts

Notation	N_2 adsorption method			XRD[a]
	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)	Particle size of Co_3O_4 (nm)
Co-Al_2O_3/ZSM-5	241.5	0.555	11.0	10.9
Co-Al_2O_3-Pt(0.05)/ZSM-5	252.5	0.572	11.2	10.8
Co-Al_2O_3-Pt(0.1)/ZSM-5	258.1	0.629	12.1	10.6
Co-Al_2O_3-Pt(0.3)/ZSM-5	262.9	0.659	11.7	10.4
Co-Al_2O_3-Pt(0.5)/ZSM-5	264.1	0.661	11.9	9.6

[a] *The particle size of Co_3O_4 is calculated by using the X-ray line broadening method with the help of Scherrer's equation*

On the other hand, Co-Al_2O_3/ZSM-5 and Co-Al_2O_3-Pt(0.05)/ZSM-5 showed one peak only at the low temperature around 422 and 321 ^oC. TPR peaks of Co-Al_2O_3-Pt(0.5)/ZSM-5 catalyst appearing at around 204 and 292 ^oC could be assigned to the easily reducible cobalt crystallites to metallic state at lower temperatures. The larger surface area and smaller crystallite size of cobalt species are found to be the characteristics of Co-Al_2O_3-Pt(0.5)/ZSM-5 catalyst, and the crystallite size of cobalt oxide and T_{max} decreased with increases in Pt content from 321 to 298 ^oC. As shown in Figure 2, the Co-Al_2O_3/ZSM-5 generates a strong cobalt-ZSM-5 interaction (relatively higher reduction temperature at around 422 ^oC) on acidic sites of ZSM-5 [18]. The temperature shift to lower values on Co-Al_2O_3-Pt(0.5)/ZSM-5 catalysts decreased with increasing Pt content.

The degree of reduction on hybrid catalysts was also calculated from the H_2 consumption values of TPR runs. The total H_2 consumption based on the weight of hybrid catalysts (denoted as total H_2 consumption/g_{cat}) are calculated as the values of 2.31, 2.29, 2.35, 2.47 and 2.46 mmol H_2/g_{cat} on Co-Al_2O_3/ZSM-5 catalysts with Pt of 0, 0.05, 0.1, 0.3, and 0.5, respectively. Increased H_2 consumption values for promoted Co-Al_2O_3/ZSM-5 catalysts compared to that of Co-Al_2O_3/ZSM-5 (2.31 mmol H_2/g_{cat}) are attributed to decrease the particle size of cobalt oxides, and total H_2 consumption increased with increasing Pt content on Co-Al_2O_3/ZSM-5 catalysts. Similarly, the absolute values of H_2 consumption up to 300 ^oC on Co-Al_2O_3/ZSM-5 catalysts at different Pt content were observed as 0.28, 0.47, 0.50, and 0.55 mmol H_2/g_{cat}, respectively. These observations also reveal the possible migration of cobalt species with a small size or ion exchange of cobalt species on the acidic sites of ZSM-5 surface. The shift of reduction temperature peak to lower region with the increased content of Pt also supports the easily reducibility of cobalt crystallites deposited on ZSM-5.

NH_3-TPD experiments were carried out to investigate the concentrations of acidic sites and their strengths on promoted Co-Al_2O_3/ZSM-5 catalysts. The acidic sites on ZSM-5 could act as the active sites for the olefin cracking reaction of FTS products even at low reaction temperatures [19]. NH_3-TPD patterns on hybrid catalysts are shown in Figure 3, and two characteristic stages of NH_3 desorption are observed with the peaks being assigned to peaks of I, II, and III according to the desorption temperatures such as peak I for NH_3 desorption temperature below 220 ^oC, peak II for 220-470 ^oC and broad peak III for above 470 ^oC. The desorption peaks of III observed at above 470 ^oC are possibly attributed to water desorption from the framework of zeolite or NH_3 decomposition [17], whereas the first peak of I at 120-220 ^oC could be assigned to weak acid sites or physically adsorbed am-

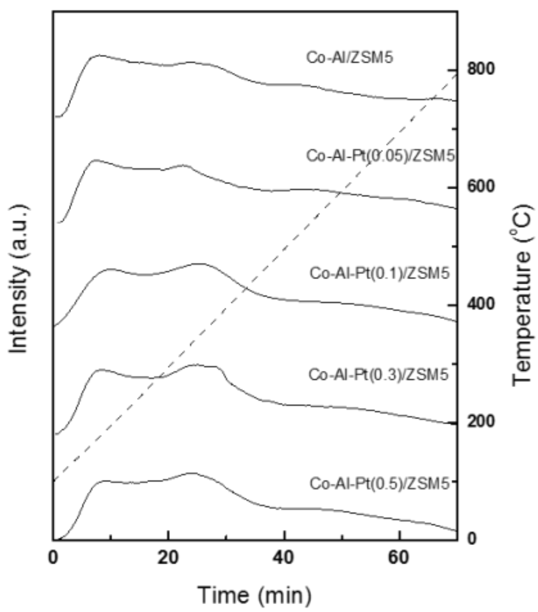


Figure 3. NH_3-TPD profiles of fresh Co-Al_2O_3/ZSM-5 and Pt promoted Co-Al_2O_3/ZSM-5 catalysts

Table 2. H_2 uptake of Co/Al_2O_3-(promoter)/ZSM5 catalysts measured by H_2-TPR

Notation	H_2 uptake, mmol H_2/g (degree of reduction, %)		
	Below 300 ^oC	Above 300 ^oC	Total uptake
Co-Al_2O_3/ZSM-5	0.26 (11.1)	2.06 (88.9)	2.31
Co-Al_2O_3-Pt(0.05)/ZSM-5	0.28 (12.23)	2.17 (87.77)	2.29
Co-Al_2O_3-Pt(0.1)/ZSM-5	0.47 (19.83)	1.88 (80.17)	2.35
Co-Al_2O_3-Pt(0.3)/ZSM-5	0.50 (20.33)	1.97 (79.67)	2.47
Co-Al_2O_3-Pt(0.5)/ZSM-5	0.55 (22.17)	1.91 (77.83)	2.46

monia, and the second peak of II at 220-470 °C is likely due to strong acidic sites [20]. Table 3 gives the acid site density expressed as mmol NH_3/g_{cat} on CoZ catalysts in terms of weak and strong acidic sites. By just considering the first and second peaks (weak and strong acid sites), which could be the active sites for the olefin cracking reaction, we observe that the acid site density is found to be higher on Co-Al_2O_3-Pt(0.1)/ZSM-5 catalyst. However, the total acid site density varies in the order of Pt(0.5) > Pt(0.3) > Pt(0, 0.05, or 0.1) with the increasing the Pt content as a promoter in FTS as summarized in Table 3.

3.3 CO conversion and product distribution

Catalytic performances of promoted Co-Al_2O_3/ZSM-5 catalysts were measured at the reaction conditions of P = 2.0 MPa, SV = 3,000 ml/gcat/h and H_2/CO = 2 for over 40 h at a somewhat higher temperature of 240 °C to elucidate the potential ZSM-5 contribution on the olefin cracking of FTS products. CO conversion and product distribution on promoted Co-Al_2O_3/ZSM-5 catalysts are presented at steady-state average values of CO conversion and product distribution after 30 h. In general, the catalyst having a large surface area with a large pore diameter is beneficial for obtaining a small cobalt crystallite size and facile transport of heavy hydrocarbons formed during FTS reaction. The large pores on FTS catalysts have been suggested to be linked to less coke or wax deposition [22]. The high content of weak acidic sites is also responsible for high yields to C_5-C_9 hydrocarbons, due to the possible catalytic cracking of higher molecular-weight olefins on acidic sites of zeolites [18,19]. As reported in our previous work, the physically-mixed iron-based FTS catalyst with ZSM-5 showed a high selectivity to byproducts and a low selectivity to olefinic hydrocarbons [22].

The conversion, selectivity and yield data of the hybrid catalysts are presented in Table 4. CO conversion proportionately increases with increasing Pt content and the trend correlates with the crystallite size of cobalt oxides and its reducibility as shown in Table 1. Also, the C_5> yield with increasing Pt content increased generally. As a result, the added Pt was the role to enhance the Fischer-Tropsch synthesis by reducing the particle size of the cobalt oxides, so Co-Al_2O_3-Pt(0.5)/ZSM-5 catalyst showed higher CO conversion and yield of C_{5+}. The Co-Al_2O_3-Pt(0.5)/ZSM-5 catalyst shows the highest CO conversion of 44.5 % and the yield of C_5-C_9 (25.9 %) showed the maximum value on Co-Al_2O_3-Pt(0.3)/ZSM-5. This reduced selectivity towards lighter hydrocarbons could be correlated with the suppressed olefin cracking properties of heavy olefin products due to the presence of less number of acidic sites [11]. Also, the presence more number of weak acidic sites (assigned to first peak in NH_3-TPD experiments) on Co-Al_2O_3-Pt(0.3)/ZSM-5 catalyst seems to be responsible for obtaining high selectivity to C_5-C_9 hydrocarbons.

The SEM technique was used to observe the influence of Pt contents different on the surface morphology. The morphology of Co-Al_2O_3-Pt(0.05, 0.1, and 0.3)/ZSM-5 catalysts can be showed Co-Al_2O_3-Pt dispersed on ZSM-5 in Figure 4, but that of Co-Al_2O_3-Pt(0.5)/ZSM-5 catalyst was well dispersed enough to not be able to observe the surface of ZSM-5. From this result, although the Co-Al_2O_3-Pt(0.5)/ZSM-5 catalyst has the higher CO conversion, the selectivity of C_5-C_9 hydrocarbons was decreased by relatively low weak acidic sites.

Figure 5 shows the variation of CO conversion and C_{10}> hydrocarbon yield with increasing Pt content in Co-Al_2O_3/ZSM-5 catalyst. The increase with Pt content is responsible for high CO conversion, due to the small particle size of cobalt oxides. On the other hand, the yields to C_5-C_9 yield was showed the maximum value on Co-Al_2O_3-Pt(0.3)/ZSM-5 catalyst. Thus, the Co-Al_2O_3/ZSM-5 catalyst with Pt improved the selectivity and yield of the C_{10}> hydrocarbon

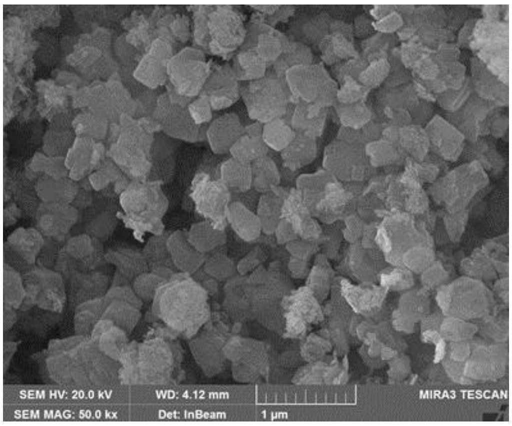
Table 3. Surface acidity of Co/Al_2O_3-(promoter)/ZSM5 catalysts by NH_3-TPD

Notation	Acidic site (mmol NH_3/g)		
	First	Second & Third	Total
Co-Al_2O_3/ZSM-5	0.018	0.035	0.053
Co-Al_2O_3-Pt(0.05)/ZSM-5	0.018	0.036	0.054
Co-Al_2O_3-Pt(0.1)/ZSM-5	0.021	0.032	0.053
Co-Al_2O_3-Pt(0.3)/ZSM-5	0.019	0.037	0.056
Co-Al_2O_3-Pt(0.5)/ZSM-5	0.018	0.039	0.057

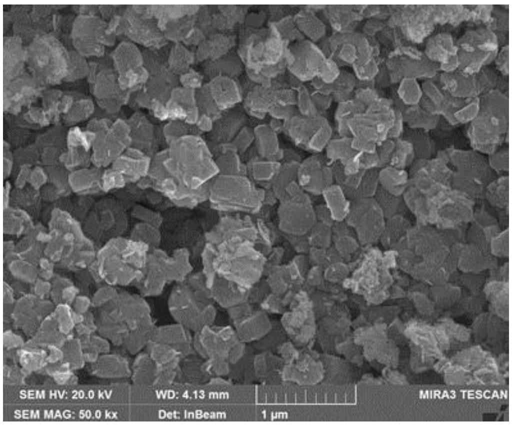
Table 4. CO hydrogenation[a] over Co/Al_2O_3-(promoter)/ZSM-5 catalysts

Pt content items	$Co-Al_2O_3$/ZSM-5	$Co-Al_2O_3Pt(0.05)$/ ZSM-5	$Co-Al_2O_3Pt(0.1)$/ ZSM-5	$Co-Al_2O_3Pt(0.3)$/ ZSM-5	$Co-Al_2O_3Pt(0.5)$/ ZSM-5
CO Conversion (%)	32.8	33.4	38.6	41.3	44.5
Selectivity (C mol %)					
CO_2	1.6	1.1	0.8	0.7	0.7
- HC -	98.4	98.9	99.2	99.3	99.3
Hydrocarbon distribution (C, mol %)					
C_1	21.9	18.7	15.2	14.2	14.3
C_2-C_4	26.1	28.4	14.2	10.3	11.4
C_5-C_9	16.9	17.2	19.7	21.8	15.6
C_{10}>	35.1	36.6	50.9	53.7	58.7
Selectivity & Yield (%)					
Selectivity: O/(O+P) [b]	33.7	31.5	19.8	17.9	16.2
Yield of C_5-C_9 & C_{10}>	11.3	12.1	19.5	21.8	15.6
	16.8	17.8	27.0	53.7	58.7

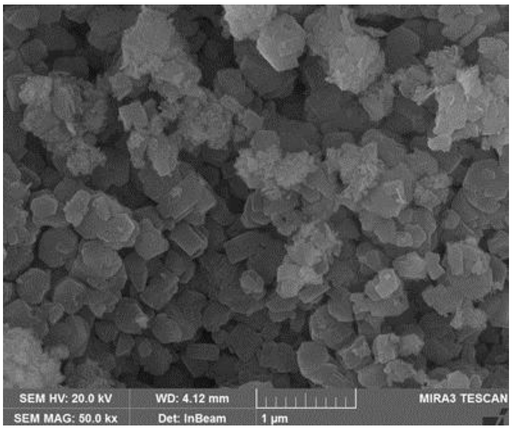
[a] *CO hydrogenation was carried out at $H_2/CO = 2$, SV = 4,000 mL/g·h and P = 2.0 MPa*
[b] *Olefin selectivity (denoted as O(olefin)/(O(olefin)+P(paraffin))) in the range of C_2-C_4 hydrocarbons*



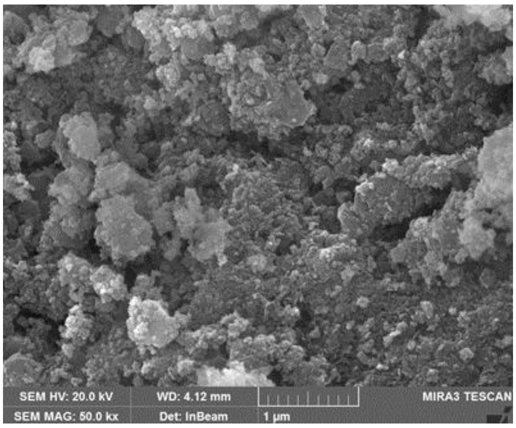
(a) $Co-Al_2O_3$-Pt(0.05)/ZSM-5



(b) $Co-Al_2O_3$-Pt(0.1)/ZSM-5



(c) $Co-Al_2O_3$-Pt(0.3)/ZSM-5



(d) $Co-Al_2O_3$-Pt(0.5)/ZSM-5

Figure 4. SEM images of the fresh Pt promoted $Co-Al_2O_3$/ZSM-5 catalysts

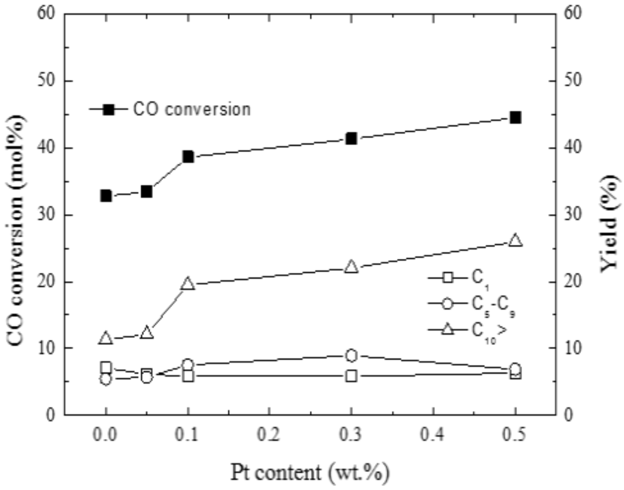


Figure 5. Correlation between the Pt content and the yield of hydrocarbons

due to higher reducibility and concentration of weak acid sites.

4. Conclusions

The CO conversion and hydrocarbons yield during FTS reaction of the hybrid catalysts were obtained to the different results according to the Pt content. The $Co\text{-}Al_2O_3\text{-}Pt(0.5)/ZSM\text{-}5$ hybrid catalyst offers higher CO conversion and C_{10+} yield, but the hybrid catalyst with Pt of 0.3 wt.% showed the maximum value for C_5-C_9 selectivity. The reducibility of cobalt particles and the concentration of weak acid sites are higher, thus consequently increasing CO conversion and C_{5+} selectivity. The presence of weak acid with large pore size and pore volume, and small cobalt particle size are mainly responsible for showing a high catalytic performance due to the high reducibility of cobalt particles.

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